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【List of the Annexed Documents】

【Document】 Specification One copy

【Document】 Abstract One copy

【Proof】 Requested

【Document】 SPECIFICATION

【Title of the Invention】 PHOTOSENSITIVE RESIN SIGNBOARD

【What is Claimed is】

【Claim 1】 A signboard comprising a support, an adhesive layer and a relief formed on at least said support via the adhesive layer, which relief is obtained from a photosensitive resin laminate having a photosensitive resin layer of not less than 500 μ, which signboard further comprises a coating layer, having an ultraviolet transmission at 400 nm of not more than 50%, on a surface thereof.

【Detailed Description of the Invention】

【Technical Field to which the Invention Pertains】

The present invention relates to a signboard made of a photosensitive resin, which is used for signboards such as display panel, decoration shield, name plate, Braille board and the like. Particularly, the present invention provides a signboard superior in resistance to light.

【Prior Art】

Signboards using photosensitive resin exposed to light through a pattern and thereafter developed to produce a photosensitive resin laminate have been conventionally disclosed in JP-A-58-55927, JP-A-9-6267 and the like and used for display panels having a relief, signboards containing Braille and the like.

However, there is a demand in the market with regard to signboards in these days for bending processing during processing of signboards, producing transparent signboards and the like. However, even if a photosensitive resin layer and a support are transparent and colorless, when placed near a window, they are colored due to the UV light, thus posing a problem.

【Problems to be Solved by the Invention】

It is therefore an object of the present invention to provide a signboard using a photosensitive resin composition

usable for display panel, decoration shield, name plate, Braille board and the like, which signboard has superior resistance to light, and which shows lower degrees of coloring by UV.

【Means of Solving the Problems】

The present inventors have conducted intensive studies in an attempt to solve the above-mentioned problems and completed the present invention. That is, the present invention provides a signboard comprising a support, an adhesive layer and a relief formed on said support via the adhesive layer, which relief is obtained from a photosensitive resin laminate having a photosensitive resin layer of not less than 500 μ, which signboard further comprises a coating layer, having an ultraviolet transmission at 400 nm of not more than 50%, on a surface thereof.

【Embodiment of the Invention】

The present invention is now explained in more detail.

The coating layer in the present invention should show an ultraviolet transmission at 400 nm of not more than 50%, preferably not more than 40%, particularly preferably not more than 35%.

To make the aforementioned ultraviolet transmission not more than 50% in the present invention, for example, a coating layer capable of absorbing the UV light may be formed on the surface of a signboard having a relief. As the coating layer, a commercially available coating agent can be used, which is specifically acrylic polymer, urethane polymer and the like.

For absorption of UV light, a low molecular weight ultraviolet absorber may be added to the coating layer, a polymer having a UV-absorbing functional group introduced therein may be added or other method may be employed. Examples of the ultraviolet absorber include 2-aminobenzophenone and the like having benzene as a skeleton, propylene glycol 2-hydroxy-3-naphthoic acid ester and the like having naphthalene

as a skeleton, 9-anthracenemethanol and the like having an anthracene skeleton, dihydrothio-p-toluidine and the like having a benzthiazole skeleton and the like. Of these, benzophenone compounds and dihydrothio-p-toluidine are preferable.

The addition of an ultraviolet absorber to the above-mentioned coating layer and a most suitable amount of the UV-absorbing functional group to be introduced into the polymer components can be determined as appropriate depending on the ultraviolet transmission at 400 nm.

While the thickness of the above-mentioned coating layer can be determined as appropriate depending on the ultraviolet transmission at 400 nm, it is preferably 5 - 300 μ, and desirably 10 - 200 μ. When it is less than 5 μ, the film strength of the coating layer becomes insufficient, whereas when it exceeds 300 μ, uniform coating without cissing becomes unpreferably difficult.

A coating layer can be formed on the surface of a signboard by a known coating method such as brushing, roller coating, spraying, dipping and the like.

The coating layer in the present invention may be directly applied on the surface of a relief made of a photosensitive resin layer, or a different layer (e.g., colored layer and the like) may be formed between a relief and a coating layer, or a different layer may be formed on the coating layer. Moreover, the aforementioned colored layer may act as a coating layer.

The present invention is explained in more detail in the following.

As the thickness of the support used in the present invention, a thickness generally in the range of 1 mm - 10 mm is employed depending on the use and design. When the support has a thickness of less than 1 mm, the support itself may warp easily, which is not suitable for signboard use, whereas a

thickness exceeding 10 mm is unpreferable because the plate does not cut easily and weighs too much.

The support usable in the present invention preferably has a Shore D hardness of not less than 35°, more preferably not less than 55°, particularly desirably 75°. When Shore D hardness is less than 35°, the support itself may warp, thus unpreferably lacking the retention performance as a signboard.

To use the support used in the present invention for Braille, for example, the support preferably has a thickness of not less than 500 μ, more preferably 800 - 1200 μ. When the thickness exceeds 120 μ, image reproductivity of the support decreases, which is not preferable.

As the support to be used in the present invention, a commercially available resin or metal can be used, and the support is preferably transparent in view of design, and has a total light transmission of not less than 60%, preferably not less than 65%, particularly preferably not less than 70%. When the total light transmission is less than 60%, the support fails to provide a good taste after processing into a signboard and is unsuitable for a signboard having a superior design.

Examples of the commercially available transparent resin for the support used in the present invention include polyester resins such as polycarbonate resin, polyethylene terephthalate resin and the like, acrylic resins such as polymethylmethacrylate and the like, copolymer resin of polymethylmethacrylate and styrene, modified polyethylene terephthalate resin obtained by copolymerization of dicyclohexanedimethanol and the like, and the like. For improved quality such as transparency, these resins may be modified by copolymerization or blending or modified by adding an additive such as a plasticizer and the like.

The photosensitive resin layer to be used in the present invention may be known, and is exemplified by a soluble

polymer compound (e.g., poly(vinyl alcohol), polyamide, polyether ester amide, polyether amide, polyurethane and the like), photopolymerizable or photocrosslinkable monomer (e.g., acrylate of polyhydric alcohol, epoxy acrylate of polyhydric alcohol, N-methylolacrylamide and the like), photopolymerization initiator (e.g., benzyldimethyl ketal, benzoindimethyl ether and the like), and a photosensitive resin composition containing, where necessary, a stabilizer, a plasticizer, a surfactant, an ultraviolet absorber and the like.

The signboard of the present invention can be produced by applying the adhesive to be mentioned later on the aforementioned support and laminating a photosensitive resin layer by a known method, and by a method of producing an ordinary printing plate to be mentioned later. As a known method of producing photosensitive resin laminate, an optional method such as heat press, injection molding, melt extrusion, solution casting, lamination and the like can be used to laminate the signboard on the support mentioned above.

The aforementioned photosensitive resin layer may be laminated in advance on, for example, a resin film of polyethylene terephthalate and the like as a support (hereinafter to be referred to as a photosensitive resin laminate precursor) and, when preparing a signboard therefrom, it is laminated on the resin support upon peeling off of the resin film.

The aforementioned photosensitive resin laminate precursor can be prepared by a method generally employed for forming a photosensitive resin laminate for a printing plate. For example, a photosensitive resin layer precursor comprising a photosensitive resin layer, a slip coat layer and a cover film disposed between the aforementioned resin film (preferably without adhesiveness in this case), and a 125 μm-thick polyester cover film having a layer of non-adhesive

transparent polymer that can be dispersed or dissolved in a developing solution [(poly(vinyl alcohol), celluloses and the like, which is also called a slip coat layer)] in a thickness of 1 - 3 μm, can be obtained.

In the present invention, the adhesive layer used for adhering a photosensitive resin layer (optionally having a slip coat layer and a cover film) to the aforementioned resin support may be a known adhesive. Examples thereof include polyester urethane adhesives wherein a soluble polyester is cured with polyhydric isocyanate, epoxy adhesives and the like. Of these, polyester urethane adhesive is preferable because it is superior in the adhesion to a photosensitive resin. Of the polyester urethane adhesives, particularly an adhesive comprising polyester and isocyanurate type polyhydric isocyanate is desirable because it dries at a low temperature.

The adhesive layer composition may contain small amounts of other components. Examples of the additive include plasticizer, dye, ultraviolet absorber, halation preventive, surfactant, photopolymerizable vinyl monomer and the like.

An adhesive layer is formed on a support typically by applying a solution of the composition for adhesive layer in a predetermined thickness and removing the solvent. The application method may be known, such as roll coater, curtain flow coater, slit die coater, gravure coater, spray and the like. The adhesive layer after coating on a support is generally dried by blowing hot air in a drying furnace.

The drying temperature of the adhesive layer to be used in the present invention is preferably 15°C to less than 80°C, and desirably 20°C - 70°C. When it exceeds 80°C, the support unpreferably gets warped and deformed. The temperature lower than 15°C prolongs the drying time, which is also unpreferable.

The adhesive layer needs to have a thickness of 0.5 μ - 100 μ. When the thickness is not more than 0.5 μ, the adhesive power cannot be achieved between the photosensitive resin

layer and the adhesive layer, whereas when it exceeds 50 μ, the time necessary for drying the coated solution becomes problematically longer. In view of the above, the adhesive layer needs to have a thickness of 0.5 μ - 100 μ, preferably 1 μ - 50 μ.

A signboard of the present invention can be prepared from the photosensitive resin laminate comprising a supporting plate, an adhesive layer and a photosensitive resin layer, which may further have a slip coat layer and a cover film, according to a method generally used for producing printing plates. For example, a negative film having a transparent image part is closely adhered onto a photosensitive resin layer via a slip coat layer or otherwise, and an actinic ray is shot thereon to insolubilize and photocure only the exposed part. The actinic radiation is obtained from a light source generally having a wavelength of 300 - 450 nm, such as high pressure mercury lamp, ultrahigh pressure mercury lamp, metal halide lamp, xenon lamp and the like.

Then, an unexposed part is removed by dissolution in a suitable solvent, particularly neutral water in the present invention, whereby a relief plate having a clear image part is obtained. For this end, spray developing apparatus, brush developing apparatus and the like can be used.

Following the above methods, a signboard of the present invention having a relief can be produced. Various signboards can be obtained, which expands the range of use, by coloring the relief with a paint, adding a pigment to a support, drawing a pattern on the back of the support or coloring the support, adhering a decorative laminate sheet and the like.

[Examples]

The present invention is explained in detail by referring to examples. The present invention is not limited by these examples in any way. The ultraviolet transmission and light resistant test are expressed by the values measured

according to the following methods.

1) Ultraviolet transmission: Photosensitive resin compositions were cut out in 30 mm × 70 mm and the ultraviolet transmission at 400 nm was measured with a self-recording spectrophotometer (U-3210, Hitachi, Ltd.).

2) Light resistance test: Using a Sunshine Weather Meter manufactured by Suga Test Instruments Co., Ltd., the specimen was irradiated with an arc carbon lamp for 75 hours and the light resistance was evaluated.

Example 1

As a support, 2.0 mm-thick acrylic plate (polymethylmethacrylate resin) was used.

As an adhesive layer, used was a polyester urethane adhesive, and a solution of the composition for adhesive layer was prepared as follows.

A polyester resin (VYLON RV-200, 80 parts by weight, Toyo Boseki Kabushiki Kaisha) was heated and dissolved in a mixed solvent (1940 parts by weight) of toluene/methyl ethyl ketone=80/20 (weight ratio) at 80°C. After cooling, DESMODUER HL (20 parts by weight, Sumitomo Bayer Urethane), an isocyanurate type polyhydric isocyanate obtained from hexamethylene diisocyanate and toluene diisocyanate was used as an isocyanurate type polyhydric isocyanate, and triethylenediamine (0.06 part by weight) was added as a curing catalyst, after which the mixture was stirred for 10 min.

The thus-obtained solution of the composition for adhesive layer was applied on an acrylic plate having a thickness of 2.0 mm, such that a film thickness was 12 μm, cure-dried at 50°C for 20 min to give a support having an adhesive layer.

As the photosensitive resin composition to be laminated, ε-caprolactam (525 parts), nylon salt (400 parts) of N-(2-aminoethyl)piperazine and adipic acid, and nylon salt (75 parts) of 1,3-bis(aminomethyl)cyclohexane and adipic acid were

subjected to melt condensation polymerization in an autoclave to give a nylon copolymer. The obtained polymer (55 parts) was dissolved in methanol (200 parts) at 60°C, and glycidyl methacrylate (2 parts) was added. The mixture was stirred for 3 h to allow reaction of glycidyl methacrylate with the polymer terminal. To this solution was added methacrylic acid (4 parts), after which acrylate (35 parts) obtained by opening addition reaction of diglycidyl ether of glycerin and acrylic acid, N-ethyltoluenesulfonamide (5 parts), hydroquinone monomethyl ether (0.1 part) and benzyl dimethyl ketal (1.0 part) were added to give a solution of a photosensitive resin composition. This solution was cast on a polyester film coated with 2 μ poly(vinyl alcohol) having a degree of hydrolysis of 98%. Methanol was evaporated to give a photosensitive resin layer precursor having a thickness of about 800 μm.

The photosensitive resin layer precursor obtained above and a support having an adhesive layer were adhered as shown in the following. The surface of a photosensitive resin composition and the surface of a support were registered and water was poured between these surfaces. The photosensitive resin layer was press-adhered at room temperature at 25°C by passing the laminate through a rubber roller whose gap clearance had been adjusted according to the thickness of the laminate, to give a photosensitive resin laminate. The photosensitive resin laminate was stood for one day and cut into a predetermined size with a circular saw teeth cutter. A negative was placed thereon and subjected to exposure, development, drying and post-exposure treatment to form a pattern of the signboard.

Then, a coating layer (50 μ) was applied to the surface of the photosensitive resin laminate having the signboard pattern. As the coating layer, a polyester resin (VYLON RV-200, 76 parts by weight, Toyo Boseki Kabushiki Kaisha) was heated and dissolved in a mixed solvent (177 parts by weight) of

toluene/methyl ethyl ketone=80/20 (weight ratio) at 80°C. After cooling, CORONATE L (19 parts by weight, polyhydric isocyanate manufactured by NIPPON POLYURETHANE INDUSTRY CO., LTD.), dehydrothio-p-toluidine (5 parts) as an ultraviolet absorber, triethylenediamine (0.1 part by weight) as a curing catalyst and ethyl acetate (50 parts) were added and the mixture was stirred for 10 min. The obtained coating solution was applied to the surface of the pattern of the photosensitive resin laminate by a spray method, and dried at 50°C for 1 h to give a photosensitive resin signboard having a coating layer.

The obtained photosensitive resin signboard was subjected to the light resistance test for 75 h, and absorbance at 400 nm was measured. The absorbance after the light resistance test was 0.25 and the ultraviolet transmission was not more than 10%, demonstrating superior resistance to light.

Comparative Example 1

In the same manner as in Example 1 except that a coating layer was not formed on the surface of the photosensitive resin laminate having a signboard pattern, a photosensitive resin signboard was obtained, which was then subjected to a light resistance test. The absorbance at 400 nm of the photosensitive resin signboard before the light resistance test was 1.10, showing poor light resistance of the photosensitive resin signboard.

Example 2

In the same manner as in Example 1 except that 1 mm-thick modified polyethylene terephthalate resin plate obtained by copolymerizing 20% of cyclohexanedimethanol was used as a support, a photosensitive resin signboard was obtained.

The obtained photosensitive resin signboard was subjected to the light resistance test for 75 h, and absorbance at 400 nm was measured. The absorbance after the

light resistance test was 0.19, and the ultraviolet transmission was not more than 5%, demonstrating superior resistance to light.

Example 3

In the same manner as in Example 1 except that the ultraviolet absorber of the coating layer was changed to 2-amino-3-naphthoic acid, a photosensitive resin signboard was obtained.

The obtained photosensitive resin signboard was subjected to the light resistance test for 75 h, and absorbance at 400 nm was measured. The absorbance after the light resistance test was 0.22, and the ultraviolet transmission was not more than 10%, demonstrating superior resistance to light.

Example 4

In the same manner as in Example 1 except that the ultraviolet absorber of the coating layer was changed to 2-amino-benzophenone, a photosensitive resin signboard was obtained.

The obtained photosensitive resin signboard was subjected to the light resistance test for 75 h, and absorbance at 400 nm was measured. The absorbance after the light resistance test was 0.24, and the ultraviolet transmission was not more than 20%, demonstrating superior resistance to light.

【Effect of the Invention】

The photosensitive resin signboard of the present invention having the above-mentioned constitution shows only a small degree of coloring due to UV light and is superior in light resistance. Therefore, it can function as an outdoor signboard for a long time, thus greatly contributing to the industry.

【Document】 Abstract

【Summary】

【Problems】 Provision of signboards, which is used for signboards such as display panel, decoration shield, name plate, Braille board and the like, and particularly superior in resistance to light.

【Solving Means】 A signboard comprising a support, an adhesive layer and a relief formed on said support via the adhesive layer, which relief is obtained from a photosensitive resin laminate having a photosensitive resin layer of not less than 500 μ, which signboard further comprises a coating layer, having an ultraviolet transmission at 400 nm of not more than 50%, on a surface thereof.

【Main Drawing】 None